(86%) of crude *cis*-1,3-cyclopentanedipropionic acid (**2a**) which had m.p. 98–99° after one recrystallization from water. A mixture melting point of this acid with an analytical sample of *cis*-1,3-cyclopentanedipropionic acid (m.p. 100–101°) was 98–99°. A mixture melting point of this acid with an analytical sample of the *trans*-dipropionic acid (**2b**, m.p. 101–102°) was 87–92°. The infrared spectra of the two samples of *cis*-1,3-cyclopentanedipropionic acid were identical except for band intensities.

The Preparation of *o*-Amino-Substituted Arylphosphonic Acids[1]

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Received April 10, 1964

Twelve years ago we described the preparation of *o*-aminophenylphosphonic acid by the copper-catalyzed reaction between *o*-bromophenylphosphonic acid and aqueous ammonia.[2] Recently, Lukin and Kalinina[3] have reported that they were unable to prepare *o*-aminophenylphosphonic acid by this reaction but obtained instead a 41% yield of *o*-hydroxyphenylphosphonic acid. In their procedure they isolated the phosphonic acid as a copper complex which was converted to the free acid by means of hydrogen sulfide. They reported further that the acid thus obtained gave a negative test for the amino group (by diazotization and coupling) and gave carbon, hydrogen, and phosphorus analyses in reasonable agreement with the theoretical values for *o*-hydroxyphenylphosphonic acid.[4]

In view of the results reported by Lukin and Kalinina, we have re-examined the matter and have found that the phosphonic acid obtained by the procedure they described contains nitrogen and is in fact identical with the *o*-aminophenylphosphonic acid prepared by us in 1952. The properties of *o*-hydroxyphenylphosphonic acid, which has recently been prepared by an unambiguous method,[5] are quite different from those of the material described by the Russian investigators. Thus the *o*-hydroxy compound has m.p. 124–127°, is extremely soluble in water, and gives a purple color with aqueous ferric chloride; by contrast, the acid described by Lukin and Kalinina has m.p. 178–179°, is only moderately soluble in water, and gives an orange-brown color with ferric chloride. Their inability to diazotize their material is surprising, since Miyata[6] has recently obtained an azo compound by diazotizing *o*-aminophenylphosphonic acid (prepared by the amination of *o*-bromophenylphosphonic acid with aqueous ammonia) and coupling the resulting diazonium salt with chromotropic acid.

Although Lukin and Kalinina are therefore mistaken about the identity of the phosphonic acid they obtained, their method of isolation is highly recommended. It is more convenient and gives more consistent results than the tedious isolation procedure we originally described.[2] Other *o*-amino-substituted arylphosphonic acids can also be isolated as copper complexes. Thus we have prepared two new compounds, 2-amino-4-tolyl- and 2-amino-5-tolylphosphonic acids, and found that they form insoluble copper complexes. It is of interest that Lukin, Kalinina, and Zavarikhina[7] have reported that 2-amino-5-chlorophenylphosphonic acid can be isolated as a copper complex; compounds in which the amino group is *meta* or *para* to the phosphono (PO_3H_2) group apparently do not form insoluble copper complexes.[8]

In the course of this work, it was found that *o*-chloro-substituted arylphosphonic acids can be converted to the corresponding *o*-amino compounds under the same conditions used with the *o*-bromo-substituted arylphosphonic acids. This result is of some interest since chloro-substituted anilines (from which the phosphonic acids are made) are usually much less expensive than are the corresponding bromo-substituted anilines.

Experimental[9]

***o*-Aminophenylphosphonic Acid.**—*o*-Bromophenylphosphonic acid[10] (23.7 g.), 18 g. of freshly prepared cuprous oxide, and 400 ml. of concentrated aqueous ammonia were allowed to react under the exact conditions specified by Lukin and Kalinina.[3] On acidification of the reaction mixture to pH 4, a greenish precipitate was obtained, which was removed by filtration and dissolved in 100 ml. of 4 *N* hydrochloric acid. Hydrogen sulfide was then passed into the solution to precipitate copper sulfide. The filtrate from the copper sulfide was decolorized with charcoal and treated with solid sodium carbonate until just alkaline to congo red (pH 3.7). The light gray precipitate thus obtained was washed with cold water and then dried *in vacuo*. The yield was 10.1 g. (58%), m.p. 189–193°. Mixture melting point with authentic *o*-aminophenylphosphonic acid[2] was 190–196°.

Anal. Calcd. for $C_6H_8NO_3P$: N, 8.09; P, 17.89. Found: N, 7.91; P, 17.69.

Some of the reaction conditions described in ref. 3 are not essential to the success of the above preparation. Thus, J. T. Baker reagent grade cuprous oxide is as satisfactory as the freshly prepared material. Furthermore, it is not necessary to pass ammonia gas through the reaction mixture (as Lukin and Kalinina have specified) in order to keep the ammonia concentration constant; equally good results are obtained by simply heating the stirred mixture of phosphonic acid, cuprous oxide, and aqueous ammonia for 18 hr. at 70–80°. It has also been found that *o*-chlorophenylphosphonic acid[11] can be substituted for *o*-bromophenylphosphonic acid in the above reaction.

2-Amino-4-tolylphosphonic Acid.—2-Bromo-4-tolylphosphonic acid[12] (12.6 g.) and 9.0 g. of cuprous oxide were added to 200 ml. of aqueous ammonia (*d* 0.90) in a three-necked flask equipped with a sealed stirrer, a reflux condenser, and a thermometer. The mixture was stirred and heated at 70–80° for 18 hr. The copper complex was isolated as described above and then dissolved in 400 ml. of 4 *N* hydrochloric acid. After the

(1) This work was supported by Research Grant GM-09479 from the National Institutes of Health, U. S. Public Health Service.

(2) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 753 (1952).

(3) A. M. Lukin and I. D. Kalinina, *Zh. Obshch. Khim.*, **30**, 1597 (1960).

(4) It should be noted that the theoretical values for carbon, hydrogen, and phosphorus do not differ greatly for *o*-aminophenylphosphonic acid and *o*-hydroxyphenylphosphonic acid. The analytical results reported by Lukin and Kalinina are in satisfactory agreement with the theoretical values for *o*-aminophenylphosphonic acid.

(5) L. D. Freedman, G. O. Doak, and E. L. Petit, *J. Org. Chem.*, **25**, 140 (1960).

(6) H. Miyata, *Bull. Chem. Soc. Japan*, **36**, 127 (1963).

(7) A. M. Lukin, I. D. Kalinina, and G. B. Zavarikhina, *Zh. Obshch. Khim.*, **30**, 4072 (1960).

(8) A. M. Lukin and I. D. Kalinina, *Dokl. Akad. Nauk SSSR*, **137**, 873 (1961).

(9) Melting points were determined as previously described [G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951)]. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(10) G. O. Doak and L. D. Frreedman, *ibid.*, **75**, 683 (1953).

(11) G. O. Doak and L. D. Freedman, *ibid.*, **73**, 5658 (1951).

(12) The preparation of 2-bromo-4-tolylphosphonic acid has been previously described [L. D. Freedman, H. Tauber, G. O. Doak, and H. J. Magnuson, *ibid.*, **75**, 1379 (1953)] but was erroneously called "2-Br-5-CH_3-$C_6H_3PO_3H_2$."

copper was removed, the pH of the solution was adjusted to 3.7, whereupon the phosphonic acid crystallized from solution. The crystals were washed with cold alcohol and then dried *in vacuo*. The yield was 4.6 g. (49%), m.p. 213–215°.

Anal. Calcd. for $C_7H_{10}NO_3P$: N, 7.48; P 16.55. Found: N, 7.68; P, 16.60.

2-Amino-5-tolylphosphonic Acid.—2-Chloro-5-tolylphosphonic acid monohydrate[13] (11.2 g.) was treated with cuprous oxide and aqueous ammonia by the procedure described above. The copper complex of the amino acid was isolated, dissolved in 90 ml. of 4 *N* HCl, and then converted to the free acid. The yield was 4.4 g. (47%), m.p. 219–222°.

Anal. Calcd. for $C_7H_{10}NO_3P$: N, 7.48; P, 16.55. Found: N, 7.23; P, 16.21.

Acknowledgment.—The authors wish to acknowledge the invaluable technical assistance given by Mr. Austin C. Cooley.

(13) L. D. Freedman and G. O. Doak, *J. Org. Chem.*, **24**, 638 (1959).

Ferrocenylphosphonous Dichloride from Ferrocenylphosphinic Acid. The >PH(O) ⇌ >P(OH) Tautomerism[1]

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Received December 26, 1963

The conversion of phosphinic acids (I) to phosphonous dichlorides (III) by treatment with excess phosphorus trichloride has been considered by Frank[3] to be evidence for tautomerism involving form II. Re-

$$\underset{\text{I}}{\text{ArPH(O)OH}} \rightleftharpoons \underset{\text{II}}{\text{ArP(OH)}_2} \longrightarrow \underset{\text{III}}{\text{ArPCl}_2}$$

cently, the existence of such an equilibrium was questioned by Quin and Dysart[4] who found only one inflection in the titration curves of several examples of I including those examined by Frank,[3] and that reaction of the acids with diazomethane failed to give the diesters. They suggested that, in the formation of III, the shift to tricovalent phosphorus involves not I, but the chloro derivative, ArPH(O)Cl.

We have found that the method of Frank[3] is applicable to the conversion of ferrocenylphosphinic acid to ferrocenylphosphonous dichloride. The compound that we have used has an estimated electron density on phosphorus of such a magnitude[5] that Quin and Dysart's hypothesis[4] would predict failure to undergo the tautomeric shift. We suggest that our results, like those of Frank,[3] indicate an equilibrium involving form II, and that the results of Quin and Dysart are not inconsistent with the existence of II.[6]

It is significant that chemical and kinetic evidence point to the existence of a tautomeric equilibrium in a related system.[7,8]

$$(RO)_2P(O)H \rightleftharpoons (RO)_2POH$$

Ferrocenylphosphonous dichloride, a red-orange liquid decomposing on attempted distillation at 0.5 mm., was obtained in 53% yield. Its solubility in *n*-heptane distinguished it immediately from the phosphinic acid which was insoluble in the same solvent. The product was identified by its hydrolysis to the phosphinic acid and conversion to ferrocenylphosphonous dipiperidide, $C_5H_5FeC_5H_4P(NC_5H_{10})_2$. The air-stable dipiperidide, golden platelets with m.p. 106–107°, represents the first known phosphorus amide of ferrocene.

Experimental

Ferrocenylphosphonous Dichloride.[9]—Phosphorus trichloride (3.52 ml., 0.04 mole) was added dropwise over a period of 2 min. to a vigorously stirred slurry of 1.0 g. (0.004 mole) of ferrocenylphosphinic acid[10] in 20 ml. of benzene under nitrogen. The addition of only a few drops of phosphorus trichloride caused a sudden, complete solubilization of the acid. The solution was orange in color, no heat developed, and there was no gas evolution. Almost immediately, immiscible phosphorous acid began to appear as a dark greenish, viscous sirup adhering to the walls of the reaction flask. Stirring was continued for 0.5 hr. at room temperature.

After decantation of the orange solution, benzene and unreacted phosphorus trichloride were removed under reduced pressure (aspirator) on a steam bath. The residue, a red-orange liquid which decomposed on attempted distillation at 0.5 mm., was taken up in *n*-heptane. The orange heptane solution plus a small amount of insoluble yellowish solids were decanted from some red-orange, semisolid material adhering to the bottom of the flask. The solids, probably unreacted phosphinic acid, were removed by filtration. Sensitivity of the dichloride to hydrolysis was indicated when evaporation of films of the filtrate in air gave crystalline phosphinic acid. The solvent was evaporated from the filtrate under a stream of nitrogen leaving 0.6 g. (53%) of red-orange liquid product.

Ferrocenylphosphonous Dipiperidide.—The ferrocenylphosphonous dichloride (0.0021 mole) was dissolved without further purification in 20 ml. of *n*-heptane. The solution, which became somewhat cloudy on standing (probably as a result of some hydrolysis), was added dropwise over a period of 5 min. to a vigorously stirred solution of 0.85 ml. (0.0086 mole) of piperidine in 20 ml. of benzene protected against atmospheric moisture. Cooling was applied with an ice–bath during the addition. The orange solution in the reaction flask soon became cloudy with formation of piperidine hydrochloride. After the addition, the mixture was stirred 2 hr. at room temperature, and then filtered. The filtrate was evaporated to dryness on a steam bath. The residue, a dark orange viscous liquid which became brown-orange in color as it solidified, was extracted three times with boiling heptane, and the insoluble, brown-orange, viscous liquid was discarded. After filtration of the combined orange heptane extracts, evaporation of the solvent under an air stream gave orange crystals together with a yellow viscous liquid which gradually solidified on standing; the yield (crude) was 0.32 g. (39.5%). The product was taken up in boiling ethanol, and the solution was filtered, concentrated, and cooled to give 0.1 g. of product in the form of golden platelets, m.p. 106–107° (uncor.).

Anal.[11] Calcd. for $C_{20}H_{29}FeN_2P$: C, 62.51; H, 7.61; Fe, 14.53; N, 7.29; P, 8.06. Found: C, 62.10; H, 7.52; Fe, 14.52; N, 6.75; P, 7.93.

Further concentration and cooling of the mother liquor yielded no more product. After removal of solvent by evapora-

(1) Abstracted in part from the Ph.D. Dissertation of G. P. Sollott, Temple University, Jan., 1962. For previous publication based on this work, *cf.* ref. 10.

(2) (a) Frankford Arsenal; (b) Temple University.

(3) A. W. Frank, *J. Org. Chem.*, **26**, 850 (1961).

(4) L. D. Quin and M. R. Dysart, *ibid.*, **27**, 1012 (1962).

(5) The electron donor ability of the ferrocenyl group appears to be greater than that of *p*-methoxyphenyl; *cf.* E. M. Arnett and R. D. Bushick, *ibid.*, **27**, 111 (1962).

(6) Quin and Dysart's argument against tautomerism has now been questioned by J. Reuben, D. Samuel, and B. L. Silver, *J. Am. Chem. Soc.*, **85**, 3093 (1963).

(7) G. O. Doak and L. D. Freedman, *Chem. Rev.*, **61**, 31 (1961).

(8) D. Samuel and B. L. Silver, *J. Org. Chem.*, **28**, 2089 (1963).

(9) The method was based on A. W. Frank's procedure A, ref. 3.

(10) G. P. Sollott and E. Howard, Jr., *J. Org. Chem.*, **27**, 4034 (1962).

(11) The analysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.